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Trapping centers in undoped GaS layered single crystals

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ABSTRACT Nominally undoped *p*-GaS layered single crystals were grown using the Bridgman technique. Thermally stimulated current measurements in the temperature range 10–300 K were performed at a heating rate of 0.10 K/s. The analysis of the data revealed six trap levels at 0.05, 0.06, 0.12, 0.63, 0.71, and 0.75 eV. The calculations for these traps yielded 1.2×10^{-21}, 2.9×10^{-23}, 2.4×10^{-21}, 8.0×10^{-9}, 1.9×10^{-9} and 4.3×10^{-10} cm^2 for the capture cross sections and 1.6×10^{13}, 5.0×10^{12}, 7.3×10^{12}, 1.2×10^{14}, 8.9×10^{13} and 2.6×10^{13} cm^{-3} for the concentrations, respectively.

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1 Introduction

Gallium sulfide (GaS) is a member of the III-VI layered semiconductor family for which each layer contains two gallium and two sulfur close-packed sublayers in the stacking sequence S-Ga-Ga-S. The bonding between two adjacent layers is of the Van der Waals type, while within the layers the bonding is predominantly covalent. It is a material of much importance both in fundamental research and in technical applications because of its structural, optical, electronic and photoelectronic properties. Investigations of the optical and electrical properties of this highly anisotropic compound have revealed that it is a promising material for near-blue-light-emitting devices [1]. Aono et al. reported that in Zn-doped GaS crystals, prepared by the iodine vapor transport method, emission ($h\nu = 2.47$ eV) is due to the complex of Zn and iodine.

One of the determining factors in the eventual device performance of semiconductors is the presence of impurity and/or defect centers in the crystal. Thus, it is very useful to get detailed information on energetic and kinetic parameters of trapping centers in this semiconductor in order to obtain high quality devices.

Among the several experimental methods for determining the properties of trap centers in semiconductors, thermally stimulated current (TSC) measurements are relatively easy to perform and provide detailed information on trap states [2, 3]. In TSC experiments, traps are filled by band-to-band excitation of carriers at low temperatures using a suitable light source. If the trapped charge carriers are thermally released to the conduction (valence) band upon heating, they give rise to a transient increase in the conductivity of the sample. For the sake of convenience in the analysis, the temperature is usually raised at a constant rate. A graph of current versus temperature is called the TSC curve. A TSC curve for a single trap depth has the form of a slightly asymmetric curve with a fairly sharp maximum at a temperature which is determined by the trap depth, the capture cross section of the trap and the heating rate. If more than one type of trap is present, curves obtained by thermal stimulation may be expected to show several maximums.

Some published data on trapping levels in undoped and doped GaS crystals are available in the literature. Trap levels have been examined in *n*-type GaS single crystals using space-charge-limited current (SCLC) measurements [4]. Two electron-trapping levels at 0.57 and 0.63 eV below the conduction band were observed. TSC measurements for electron centers acting in *n*-GaS single crystals have been carried out in the range 77 to 300 K and five sets of electron traps were found [5]. A series of electron centers was found by TSC measurements for *n*-GaS grown by different methods [6]. Three electron traps were detected by TSC, SCLC and photoinduced current transient spectroscopy measurements for *n*-GaS, grown from vapor by iodine chemical transport, at 0.17, 0.45 and 0.56 eV below the conduction band [7]. A systematic investigation of trapping center parameters has been carried out on a series of GaS_xSe_{1-x} mixed crystals using TSC and SCLC measurements [8, 9]. The crystals were grown from the vapor by means of the iodine-assisted transport method.

In the present paper, we describe and analyze TSC measurements performed on nominally undoped GaS crystals. From the analysis of the experimental data, the energy, the capture cross section and concentration of the traps have been obtained. In contrast to all previous TSC measurements on GaS, we study *p*-GaS, for which we observe hole traps and employ a wide temperature range of 10–300 K. The low-temperature experiments allow us to check for the possibility of extremely shallow trap states.

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2 Experimental

Gallium sulfide polycrystals were synthesized from high-purity elements (at least 99.999%) taken in stoichiometric proportions. GaS single crystals were grown by the modified Bridgman method. The analysis of X-ray diffraction data showed that they crystallize in hexagonal unit cells with parameters: $a = 0.359$ and $c = 1.549$ nm. The GaS crystals were found to be $p-$type after measuring with a hot probe. Crystals suitable for measurements were obtained by easy cleavage perpendicular to the optical c-axis and had the dimensions $5.5 \times 7.5 \times 0.2\,\mathrm{mm}^3$. The energy band gap of GaS for indirect optical transition is 2.62 eV at 4.2 K [10].

The electrodes were deposited by evaporating gold under high vacuum, on both crystal surfaces according to the sandwich geometry. Their thicknesses were about 100 nm on the back side and 10 nm on the front side, the latter corresponding to a higher transmittance of incident light. The sample was mounted on the cold finger of a cryostat with conducting silver paste. The back side was grounded through the sample holder. A thin gold wire was attached to the front side electrode by a small droplet of silver paste. The I–V characteristics were checked to be symmetric with respect to the polarity. A bias voltage on the order of 30 V was applied to the sample.

All measurements were carried out in vacuum in a CTI-Cryogenics M-22 closed-cycle helium system and extended from 10 to 300 K with a constant heating rate of $\beta = 0.10$ K/s. The traps were filled by creating carriers using band-to-band photoexcitation of the samples. The light source was the 457.9 nm line (2.715 eV, 50 mW) of a Spectra Physics argon laser. The thermally stimulated currents were measured by a Keithley 619 electrometer. The TSC and temperature data were stored in a personal computer.

In a typical experiment, the samples were cooled down to $T = 10$ K and kept at this temperature for $\sim$10 min. Then they were illuminated through the semi-transparent front electrode for a fixed period of time ($t = 25$ min) under particular biasing conditions and left to sit for $\sim$ 10–25 min to allow the photoconductivity signal to decay after exposure to the light. The samples were then heated at a constant rate from 10 up to 300 K.

3 Results and discussion

3.1 *Determination of the type of carrier traps*

Figure 1 shows typical TSC spectra of GaS single crystals for two biasing polarities and a constant heating rate of $\beta = 0.10$ K/s in the 10–300 K temperature range. When the sample is illuminated through a semitransparent contact, both types of carriers are created near the contact. Then, depending on the bias voltage, only one type of carrier will be swept through the whole field zone, whereas the second type is collected very quickly. Therefore, only the former can be trapped [11]. As is seen from Fig. 1, all the peaks are more intense if the illumination occurs through the positively biased contact. Therefore, all of the peaks can be attributed to hole traps.

3.2 *Activation energy and cross section determination*

In order to apply the usual analytical methods for the determination of trap parameters, it is necessary to isolate

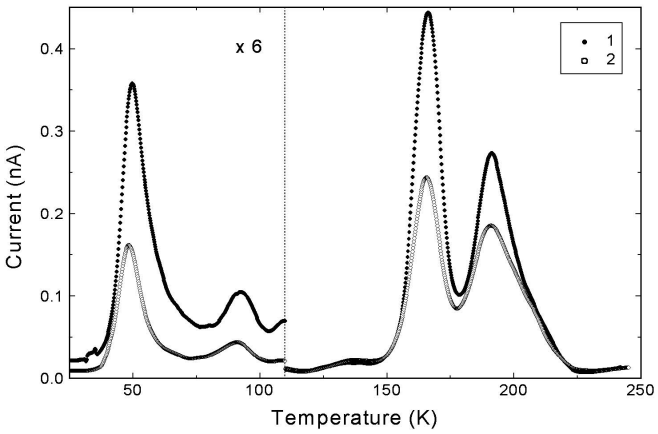

FIGURE 1 Typical TSC curves of a GaS single crystal obtained under an opposite bias voltage of 30 V. Curves 1 and 2 represent the experimental data obtained with the illumination of the positive and negative contacts, respectively. The low-temperature parts of the TSC spectra are multiplied by a factor of six

the TSC peaks. We used the curve fitting method [12] to analyze TSC spectra of the GaS crystal. This analysis indicated that eight peaks are present at 50, 67, 92, 110, 136, 166, 191, and 207 K, suggesting the presence of eight trapping centers (Fig. 2). We have analyzed only six of them. The remaining two peaks with maximums at $T = 110$ and 136 K were not analyzed, because they have very low intensities with respect to neighboring peaks. The main six peaks can be subdivided into two groups, the former including the first three peaks and the latter one with the last three peaks.

There are several methods in the literature for determining the activation energy of a trap from experimental TSC curves. We chose to use the "initial rise", Chen's and curve fitting methods.

3.2.1 "Initial rise" method. The "initial rise" method, invented by Garlick and Gibson [13] and valid for all types of recombination kinetics, is based on the assumption that, when

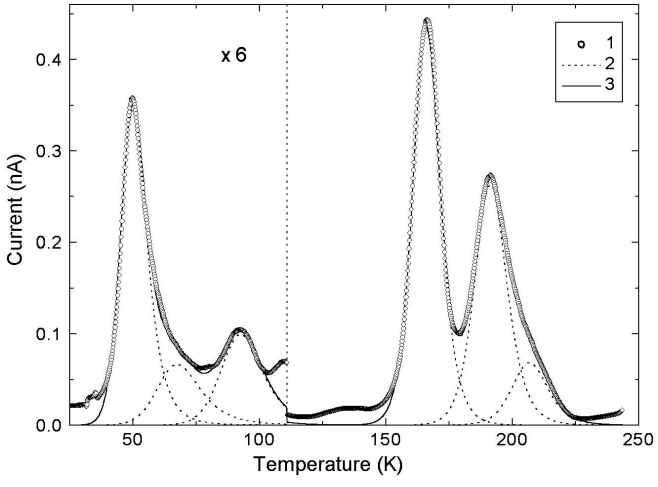

FIGURE 2 Decomposition of the TSC spectrum of the GaS crystal into six separate peaks using the conventional curve fitting method. 1, experimental data; 2, decomposed peaks, using (5) and (8); 3, total fit to the experimental data using (8). The low-temperature part of the TSC spectrum is multiplied by a factor of six

traps begin to empty as the temperature is increased, the TSC is proportional to $\exp(-E_t/kT)$. Here, E_t is the activation energy of the trap and k is Boltzmann's constant. Thus, a plot of the logarithm of the current flow against $1000/T$ yields a straight line with a slope of $-E_t$, as shown in Fig. 3. The activation energies of the traps calculated by this procedure were found to be 0.05, 0.06, 0.11, 0.61, 0.71, and 0.74 eV for the T_1–T_6 peaks, respectively (Table 1).

3.2.2 Chen's method. Chen's method requires the measurement of the low (T_l) and high (T_h) temperatures at which the TSC signal is equal to half of its maximum value. The activation energies of the trap are then given by [3, 14]

$$E_\tau = \left[1.51 + 3.0\left(\mu_g - 0.42\right)\right] kT_m^2/\tau - \left[1.58 + 4.2\left(\mu_g - 0.42\right)\right] 2kT_m ,$$

$$E_\delta = \left[0.976 + 7.3\left(\mu_g - 0.42\right)\right] kT_m^2/\delta ,$$

$$E_w = \left[2.52 + 10.2\left(\mu_g - 0.42\right)\right] kT_m^2/w - 2kT_m ,$$

where $\tau = T_m - T_l$, $\delta = T_h - T_m$, $w = \tau + \delta$, $\mu_g = \delta/w$, and T_m is the temperature corresponding to the TSC peak maximum. The activation energies E_τ, E_δ and E_w are obtained by using the half-width towards the low temperature side, the high temperature side and the total width, respectively.

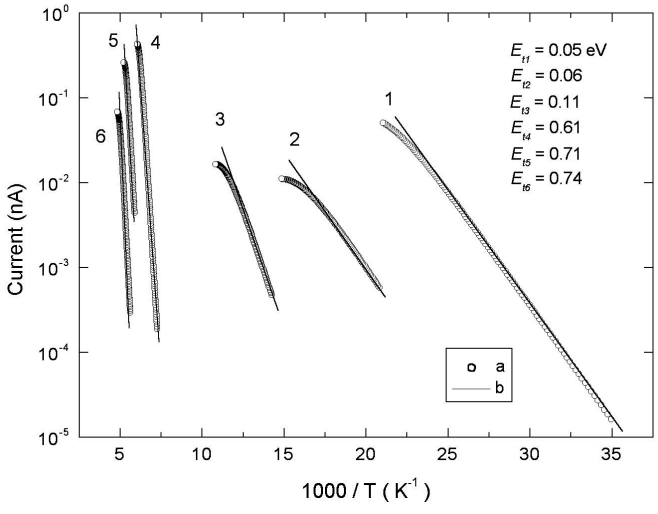

FIGURE 3 Thermally stimulated current vs. $1000/T$ for all six peaks in the TSC spectrum of the GaS crystal: **a** experimental data, **b** theoretical fits using the "initial rise" method

A value of $\mu_g = 0.42$ was predicted by Chen for first order TSC peaks and $\mu_g = 0.52$ for second order ones. The calculated values of μ_g for our decomposed peaks T_1, T_2, andT_3 were found to be 0.54, 0.55, and 0.54, respectively, and 0.51 for T_4, T_5 and T_6. Therefore our TSC peaks should be considered as second order peaks. The activation energies obtained by this method are also reported in Table 1.

3.2.3 Curve fitting method. There are three different curve fitting formulas for TSC curves depending on the relative magnitudes of the capture cross sections S_T and S_R of the trapping and recombination centers, respectively. For $S_T \ll S_R$ the process is monomolecular, i.e. no retrapping occurs. The cases $S_T = S_R$ and $S_T \gg S_R$ are bimolecular and fast retrapping, respectively. To analyze our experimental data, we have chosen the bimolecular case, which gives the best fit to our TSC curve.

Garlick and Gibson considered the case where a free electron has equal probabilities of recombining or being retrapped [13]. The resultant conductivity curve is described by

$$\Delta\sigma = \frac{n_{t0}^2 \tau \mu e \nu \exp\left(-E_t/kT\right)}{N_t\left[1 + \frac{n_{t0}}{N_t}\frac{\nu}{\beta}\int_{T_0}^{T}\exp\left(-E_t/kT'\right)\mathrm{d}T'\right]^2} . \quad (1)$$

$\Delta\sigma$is the thermally stimulated conductivity, n_{t0} the initial density of filled traps, N_t is the density of traps, τ the lifetime of a free hole, μ the hole mobility, β the heating rate and T_0 the temperature from which heating begins following the filling of the traps. ν is the attempt-to-escape frequency of a trapped hole:

$$\nu = N_c \upsilon_{th} S_t ,$$

where N_c is the effective density of states in the valence band, υ_{th} the thermal velocity of a free hole and S_t the capture cross section of the trap. If it is assumed that ν is independent of T and that over the temperature span of the TSC curve, the variation of μ and τ with T can be ignored, and that $n_{t0} = N_t$, which means that all the traps are filled, (1) can be rewritten as

$$\Delta\sigma = \frac{A\exp(-t)}{\left[1 - B\int_{t_0}^{t}\exp(-t)t^{-2}\,\mathrm{d}t\right]^2} , \quad (2)$$

Peak	T_m (K)	E_t(eV) Chen (E_τ; E_δ; E_w)	"Initial rise"	Curve fit	S_t (cm^2)	N_t(cm^{-3})
T_1	49.9	0.05; 0.06; 0.06	0.05	0.05	1.2×10^{-21}	1.6×10^{13}
T_2	67.4	0.06; 0.07; 0.06	0.06	0.06	2.9×10^{-23}	5.0×10^{12}
T_3	92.5	0.12; 0.13; 0.13	0.11	0.12	2.4×10^{-21}	7.3×10^{12}
T_4	165.9	0.63; 0.60; 0.62	0.61	0.63	8.0×10^{-9}	1.2×10^{14}
T_5	191.3	0.71; 0.68; 0.70	0.71	0.71	1.9×10^{-9}	8.9×10^{13}
T_6	206.7	0.75; 0.72; 0.74	0.74	0.75	4.3×10^{-10}	2.6×10^{13}

TABLE 1 The activation energy, capture cross section and concentration of the traps for six TSC peaks of the GaS crystal

where $t = E_t/kT$, and A and B are constants: $A = n_{t0}\tau e\mu\nu$ and $B = \nu E_t \beta k$. Repeated integrations by parts of the integral in (2) leads to a convergent infinite series, and then one obtains

$$\Delta\sigma = \frac{A\exp(-t)}{\left[1 + B\left(\exp(-t)t^{-2} - 2\exp(-t)t^{-3} + 3\times 2\exp(-t)t^{-4}...\right|_{t_0}^{t}\right]^2}. \quad (3)$$

Since t is large in practice, in the range 10–45, an approximate value for $\Delta\sigma$ can be obtained by dropping all but the first term in the series; giving

$$\Delta\sigma = \frac{A\exp(-t)}{\left[1 + B\exp(-t)\ t^{-2}\big|_{t_0}^{t}\right]^2}. \quad (4)$$

If t_0 is sufficiently greater than all values of t corresponding to the temperature span of the TSC curve, the bottom limit in (4) can also be ignored and

$$\Delta\sigma = \frac{A\exp(-t)}{\left[1 + B\exp(-t)\ t^{-2}\right]^2}. \quad (5)$$

If (5) is differentiated and equated to zero to find the maximum of the curve, which occurs when $t = t_m = E_t/kT_m$, then

$$B = \exp(t_m)\, t_m^3/(t_m + 4). \quad (6)$$

Moreover, it is possible to calculate the trapping cross-section S_t with the following expression:

$$S_t = \frac{\beta E_t}{(E_t + 4kT_m)\, N_c \upsilon_{th} k T_m^2} \exp\left(\frac{E_t}{kT_m}\right). \quad (7)$$

In the TSC spectra of GaS crystals, we analyzed six peaks, partially overlapping each other in two separate groups. Therefore, the following fit function was used:

$$\Delta\sigma = \sum_{i=1}^{6} \Delta\sigma_i. \quad (8)$$

This procedure allowed us to obtain E_t and T_m for each peak directly from the fit. Then using (7), we calculated S_t for all six peaks (Table 1).

3.3 *Trap concentration determination*

The concentration of the traps was estimated using the relation [15]

$$N_t = Q/ALeG.$$

Here Q is the quantity of charge released during a TSC experiment and can be calculated from the area under the TSC peaks; A and L are the area and the thickness of the sample, respectively; e is the electronic charge and G is the photoconductivity gain, which is equal to the number of holes passing through the sample for each absorbed photon. N_t was calculated by assuming $G = 1$ [15]. The values of N_t obtained are presented in Table 1.

4 Conclusion

TSC spectroscopy has been used to characterize traps in nominally undoped GaS layered crystals. Six distinct traps were observed in the temperature range 10 to 300 K using excitation light of 2.715 eV, a sufficiently long illumination time (∼25 min) and a heating rate of 0.10 K/s.

Energy levels of 0.05, 0.06, 0.12, 0.63, 0.71, and 0.75 eV above the valence band were determined. The activation energies of the peaks, evaluated by the curve fitting method, and also calculated using the "initial rise" and Chen's methods from the isolated peaks, are in agreement with each other, within the accuracy of the methods used. We note that this is the first time six new hole traps have clearly been identified in *p*-type GaS. The trap levels above the valence band may lead to alternative recombination pathways modifying blue emission efficiency. The capture cross sections of the traps were calculated to be 1.2×10^{-21}, 2.9×10^{-23}, 2.4×10^{-21}, 8.0×10^{-9}, 1.9×10^{-9} and 4.3×10^{-10} cm^2. The concentrations of the traps were estimated to be 1.6×10^{13}, 5.0×10^{12}, 7.3×10^{12}, 1.2×10^{14}, 8.9×10^{13} and 2.6×10^{13} cm^{-3}.

The shallow hole traps with energies 0.05, 0.06, and 0.12 eV are very probably related to vacancies of gallium. The deeper traps, having large cross sections 3.0×10^{-9}, 7.0×10^{-10} and 1.6×10^{-10} cm^2, may be associated with extended defect regions, such as stacking faults or dislocations, which are quite possible in GaS due to the weakness of the van der Waals forces between the layers.

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